**723.** *Polyfluoroarenes. Part IV.[1] 2,3,4,5,6-Pentafluorotoluene and Related Compounds.*

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Hexafluorobenzene undergoes ready reaction with alkyl-lithium compounds at low temperatures, and n-butylpentafluorobenzene and 2,3,4,5,6-pentafluorotoluene were thus prepared in good yield. Oxidation of the latter gives pentafluorobenzoic acid. Free-radical halogenation of pentafluorotoluene affords pentafluorobenzyl and pentafluorobenzylidene halides. Further halogenation leads to addition to the aromatic ring rather than formation of the benzotrihalide. 2,3,4,5,6-Pentafluorobenzyl bromide gives a Grignard compound, and reacts with thiourea, acetate ion, and potassium phthalimide with elimination of bromide ion and without extensive loss of fluoride. The compounds $C_6F_5 \cdot CH_2 \cdot OH$, $C_6F_5 \cdot CH_2 \cdot CO_2H$, $C_6F_5 \cdot CH_2 \cdot NH_2$, and $(C_6F_5 \cdot CH_2)_2$ have been synthesised, and a new polymer of structure $C_6F_5 \cdot CH_2 \cdot O \cdot [C_6F_4 \cdot CH_2 \cdot O]_n \cdot H$ has been prepared.

THE reactions of polyfluoroarenes with nucleophilic reagents have recently received considerable attention,[2-6] but only one attempt to displace nuclear fluorine by the action of a carbanion has been reported. The reaction of hexafluorobenzene with methylmagnesium iodide has been shown, by mass-spectrographic analysis of the products, to give a very low yield (3%) of 2,3,4,5,6-pentafluorotoluene.[2] The reaction of hexafluorobenzene with alkyl-lithium compounds has now been investigated, and gives good yields of alkylpentafluorobenzenes:

$$C_6F_6 + LiR \longrightarrow C_6F_5 \cdot R + LiF$$

(I)
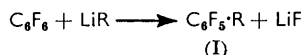
Hexafluorobenzene reacts with a slight excess of methyl-lithium in tetrahydrofuran solution at $-60°$ to give pentafluorotoluene (I; R = Me) in 70—75% yield. A similar reaction between hexafluorobenzene and n-butyl-lithium gives a 56% yield of the butyl derivative (I; R = Bu^n), with some dibutyltetrafluorobenzene (20%) which was not further investigated. Reaction between methyl-lithium and hexafluorobenzene occurs less readily in diethyl ether, but a 69% yield of pentafluorotoluene was obtained from the reaction in this solvent at $-15°$.

2,3,4,5,6-Pentafluorotoluene reacts only slowly with oxidising agents in aqueous solution; with concentrated nitric acid, alkaline potassium permanganate, or potassium dichromate in 50% sulphuric acid, attack on the ring occurs with liberation of fluoride ion. A small yield (3%) of pentafluorobenzoic acid was obtained by oxidation of pentafluorotoluene with chromium trioxide in acetic acid. Pentafluorobenzoic acid has been prepared previously by hydrolysis of octafluorotoluene with fuming sulphuric acid,[7] by oxidation of pentafluorophenylethylene with potassium permanganate in acetone solution,[8] and by carbonation of pentafluorophenylmagnesium halides.[8]

Side-chain Halogenation of Pentafluorotoluene.—2,3,4,5,6-Pentafluorotoluene undergoes free-radical halogenation to give pentafluorobenzyl and pentafluorobenzylidene halides. The peroxide-catalysed reaction of equimolar quantities of sulphuryl chloride and pentafluorotoluene appears to proceed more slowly than the corresponding reaction with toluene

[1] Part III, Birchall, Haszeldine, and Parkinson, *J.*, 1961, 2204.
[2] Pummer and Wall, *Science*, 1958, **127**, 643.
[3] Birchall and Haszeldine, *J.*, 1959, 13.
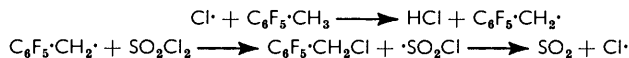[4] Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199.
[5] Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.
[6] Robson, Stacey, Stephens, and Tatlow, *J.*, 1960, 4754.
[7] McBee and Rapkin, *J. Amer. Chem. Soc.*, 1951, **73**, 1366.
[8] Nield, Stephens, and Tatlow, *J.*, 1959, 166.

itself.[9] 2,3,4,5,6-Pentafluorobenzyl chloride was produced in 34% yield, and 64% of the pentafluorotoluene was recovered unchanged. However, use of two molecular proportions of sulphuryl chloride gives 2,3,4,5,6-pentafluorobenzyl chloride (77%) and 2,3,4,5,6-pentafluorobenzylidene chloride (7%). These observations suggest that the hydrogen of the pentafluorotoluene is less susceptible to free-radical attack than that in toluene during the chain reaction:

$$Cl\cdot + C_6F_5\cdot CH_3 \longrightarrow HCl + C_6F_5\cdot CH_2\cdot$$
$$C_6F_5\cdot CH_2\cdot + SO_2Cl_2 \longrightarrow C_6F_5\cdot CH_2Cl + \cdot SO_2Cl \longrightarrow SO_2 + Cl\cdot$$

The shielding effect of a perfluoroalkyl group towards adjacent C–H bonds during chlorination is known from studies with the compounds $CF_3\cdot CH_3$ and $CF_3\cdot CH_2\cdot CH_3$.[10]

The results of experiments in which 2,3,4,5,6-pentafluorotoluene and chlorine were irradiated by a powerful source of ultraviolet light are summarised in Table 1. All irradiations were continued until the chlorine was completely consumed.
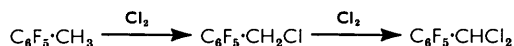
TABLE 1. *Chlorination of pentafluorotoluene.*

Reactant ratio $Cl_2 : C_6F_5\cdot CH_3$	Reaction time (hr.)	HCl *	Products (mole %)			Products of higher b. p.†
			$C_6F_5\cdot CH_3$ †	$C_6F_5\cdot CH_2Cl$ †	$C_6F_5\cdot CHCl_2$ †	
1 : 1	3	91	21	63	9	3—4
2 : 1	12	75	—	30	43	*ca.* 22
3 : 1	20	67	—	—	43	*ca.* 45

* Based on chlorine. † Based on pentafluorotoluene.

Infrared spectroscopic examination of the products of higher b. p. listed in Table 1 revealed strong bands in the 1700 cm.$^{-1}$ region, attributed to formation of methyl penta-fluoro-cyclohexenes and -cyclohexadienes by addition of chlorine to the aromatic ring. The virtual absence of an aromatic ring is these products was shown by the very weak absorption in the region (1500 cm.$^{-1}$) where pentafluorophenyl compounds absorb strongly. In particular, pentafluorobenzotrichloride was not isolated or detected and it is doubtful whether it was formed at all.

The quantity of hydrogen chloride liberated (67%) in the experiment employing three molecular proportions of chlorine, and the absence of pentafluorobenzotrichloride from the products of chlorination of pentafluorotoluene, shows that little, if any, elimination of the final hydrogen atom from pentafluorobenzylidene chloride took place under the conditions employed.

Substitution in side-chain:

$$C_6F_5\cdot CH_3 \xrightarrow{Cl_2} C_6F_5\cdot CH_2Cl \xrightarrow{Cl_2} C_6F_5\cdot CHCl_2$$

Addition to nucleus:

$$C_6F_5\cdot CHCl_2 \xrightarrow{Cl_2} C_6F_5Cl_2\cdot CHCl_2 \xrightarrow{Cl_2} C_6F_5Cl_4\cdot CHCl_2, \text{ etc.}$$

1,2,3,4,5,6-Hexachlorohexafluorocyclohexane and 1,2,3,4,5,6-hexachloropentafluoro-cyclohexane have been isolated from the photochemical chlorination of hexafluoro-benzene [4] and pentafluorobenzene,[8] respectively, demonstrating that attack on the nucleus is feasible.

2,3,4,5,6-Pentachlorobenzylidene chloride is also resistant to further substitution by chlorine, and this has been attributed to steric hindrance by the chlorine atoms *ortho* to the dichloromethyl group.[11] Examination of molecular models indicates that steric

[9] Kharasch and Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 2142.
[10] Henne and Whaley, *J. Amer. Chem. Soc.*, 1942, **64**, 1157.
[11] Ballester and Molinet, *Chem. and Ind.*, 1954, **73**, 1290.

considerations may also apply in the case of pentafluorobenzylidene chloride, but are less important than for the perchloro-compound. 2,4,6-Trifluoromesitylene undergoes complete chlorination at high temperatures, but only a small yield of 2,4,6-trifluorotris-(trichloromethyl)benzene is obtained, and there is appreciable replacement of methyl groups by chlorine.[12]

Free-radical bromination of 2,3,4,5,6-pentafluorotoluene also readily proceeds to the monosubstitution stage, and an 85% yield of 2,3,4,5,6-pentafluorobenzyl bromide is obtained without difficulty. 2,3,4,5,6-Pentafluorobenzyl chloride and bromide, particularly the latter, are markedly lachrymatory.

Pentafluorobenzyl Alcohol.—In view of the relatively high reactivity of fluorine in the polyfluoroarene ring towards nucleophilic reagents, the preparation of compounds containing the pentafluorobenzyl group by nucleophilic displacement of only the benzyl halogen atom from pentafluorobenzyl halides necessitates a careful choice of reagents. The pentafluorobenzyl halides are readily characterised by conversion into the S-(2,3,4,5,6-pentafluorobenzyl)thiouronium picrate.

Despite this ready replacement of bromine by thiourea in ethanolic solution, 2,3,4,5,6-pentafluorobenzyl bromide reacts only slowly with aqueous potassium hydroxide; fluoride and bromide ions are liberated, and the principal product is an alkali-insoluble solid. This material, on the basis of elemental analysis and infrared spectroscopy, is probably a polymer built up from pentafluorobenzyl alcohol by stepwise nucleophilic attack, as illustrated.
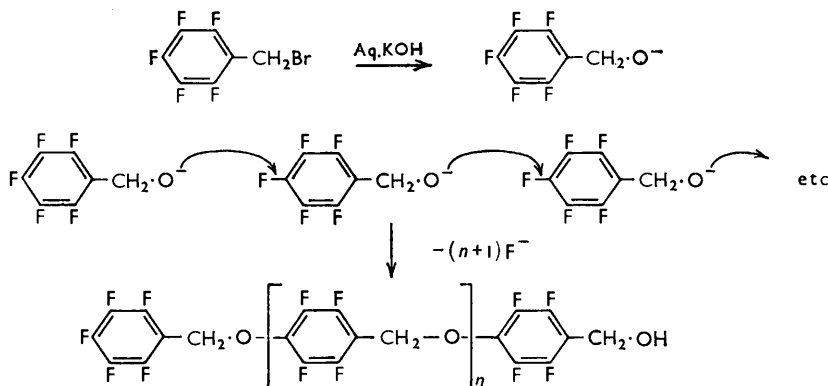
Elimination of bromide without loss of fluoride from pentafluorobenzyl bromide is achieved by reaction with potassium acetate in acetic acid solution, which gives an 83% yield of 2,3,4,5,6-pentafluorobenzyl acetate. The latter undergoes slow acid-catalysed hydrolysis to pentafluorobenzyl alcohol. The difficulty in separation, by distillation, of the benzyl alcohol from unchanged acetate would be overcome if reaction were carried out on a larger scale than employed during the present work.

Pentafluorophenylacetic Acid.—Pentafluorobenzyl bromide reacts readily with magnesium in ether, and carbonation of the resulting solution gives a low yield (14%) of (pentafluorophenyl)acetic acid, characterised as its S-benzylthiouronium salt. The main product is 1,2-bispentafluorophenylethane (59%); the tendency of substituted benzyl halides to form coupled products of this type during the preparation of Grignard compounds is well known.[13]
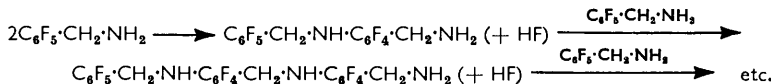
Pentafluorobenzylamine.—Some fluoride ion was liberated when 2,3,4,5,6-pentafluoro-benzyl bromide was heated with potassium phthalimide, but a 70% yield of N-(2,3,4,5,6-pentafluorobenzyl)phthalimide was obtained. Conversion of the substituted phthalimide

[12] Finger, Reed, Maynert, and Weiner, *J. Amer. Chem. Soc.*, 1951, **73**, 149.
[13] Humphlett and Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 3289.

into 2,3,4,5,6-pentafluorobenzylamine (76% yield) was readily achieved by reaction with hydrazine hydrate, and the amine was characterised as its benzoyl derivative.

2,3,4,5,6-Pentafluorobenzylamine is stable for long periods at $-78°$, but a white solid separates when the amine is kept at room temperature or when it is distilled under atmospheric pressure. The solid is soluble in water to give a solution containing fluoride ion and is probably formed by stepwise nucleophilic attack of the amine on the pentafluorophenyl ring in another molecule.

$$2C_6F_5 \cdot CH_2 \cdot NH_2 \longrightarrow C_6F_5 \cdot CH_2 \cdot NH \cdot C_6F_4 \cdot CH_2 \cdot NH_2 \ (+ \ HF) \xrightarrow{C_6F_5 \cdot CH_2 \cdot NH_2}$$
$$C_6F_5 \cdot CH_2 \cdot NH \cdot C_6F_4 \cdot CH_2 \cdot NH \cdot C_6F_4 \cdot CH_2 \cdot NH_2 \ (+ \ HF) \xrightarrow{C_6F_5 \cdot CH_2 \cdot NH_2} \text{etc.}$$

Displacement of fluorine from the polyfluoroarene ring by the attack of amines is now well established.[5]

2,3,4,5,6-Pentafluorobenzylamine is sparingly soluble in water, and gives a solution which is alkaline to Methyl Red. Its ionisation constant (Table 2) shows it to be a much weaker base then benzylamine. The inductive electron-withdrawing power of the C_6F_5 group is thus less than that of CF_3, and of the same order as for CHF_2 or CO_2Et.

TABLE 2. *Ionisation constants* (K_b) *at* $25°$.

$C_6F_5 \cdot CH_2 \cdot NH_2$	$5 \cdot 0 \times 10^{-7}$	$CF_3 \cdot CH_2 \cdot NH_2$ [16]	$5 \cdot 3 \times 10^{-9}$
$C_6H_5 \cdot CH_2 \cdot NH_2$ [14]	2×10^{-5}	$CHF_2 \cdot CH_2 \cdot NH_2$ [17]	$3 \cdot 3 \times 10^{-7}$
$EtO \cdot CO \cdot CH_2 \cdot NH_2$ [15]	5×10^{-7}		

2,2,2-Trifluoroethylamine [18] and glycine ester [19] yield stable diazo-compounds on treatment with nitrous acid, and it was of interest to determine whether 2,3,4,5,6-pentafluorobenzylamine would react similarly. However, attempts to nitrosate pentafluorobenzylamine gave only 2,3,4,5,6-pentafluorobenzyl alcohol (28%) and 2,3,4,5,6-pentafluorobenzyl chloride (25%). Although the electron-attraction and benzenoid resonance of the pentafluorophenyl group might be expected to facilitate loss of a proton from the diazonium intermediate (II) [path (a)] to yield the pentafluorophenyldiazomethane, the mesomeric effect of the aromatic fluorine could assist in stabilising the pentafluorobenzyl carbonium ion if this were formed by elimination of nitrogen [path (b)]. Mesomeric electron release from fluorine in polyfluoroarenes has been noted previously.[20]
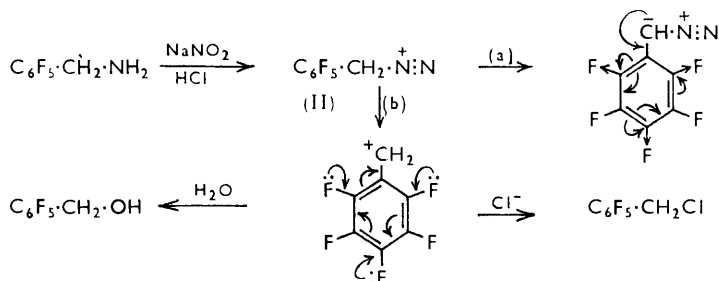
Spectra.—Compounds derived from the 2,3,4,5,6-pentafluorotoluene system show a very strong doublet at approximately 1500 cm.$^{-1}$, and a sharp band, of weak—medium intensity, at ~ 1660 cm.$^{-1}$. These bands, which show little variation in frequency or

[14] Lange (ed.), " Handbook of Chemistry," Handbook Publ. Inc., Ohio, 9th edn. (1956), p. 1202.
[15] Neuberger, *Proc. Roy. Soc.*, 1937, *A*, **158**, 68.
[16] Stewart, *Diss. Abs.*, 1958, **18**, 801.
[17] Washburn (ed.), " International Critical Tables." McGraw-Hill Book Co., New York, 1929, Vol. V, p. 262.
[18] Gilman and Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1458.
[19] Silberrad, *J.*, 1902, **81**, 600.
[20] Birchall and Haszeldine, *J.*, 1959, 3653.

strength with modification of the side-chain, are listed in Table 3. The 1500 cm.$^{-1}$ doublet is assigned to skeletal vibrations of the pentafluorophenyl ring (in accordance with the assignment for the similar bands in the spectra of hexafluorobenzene and compounds containing the $C_6F_5 \cdot O \cdot$ group [3]). The strength and position of the doublet are such that it

TABLE 3. *Infrared bands.*

	Doublet near 1500 cm.$^{-1}$	Band near 1660 cm.$^{-1}$		Doublet near 1500 cm.$^{-1}$	Band near 1660 cm.$^{-1}$
$C_6F_5 \cdot CH_3$	1502, 1522	1656	$C_6F_5 \cdot CH_2Br$	1508, 1522	1656
$C_6F_5 \cdot C_4H_9{}^n$	1504, 1520	1656	$C_6F_5 \cdot CH_2 \cdot OH$	1504, 1520	1661
$(C_6F_5 \cdot CH_2)_2$ *	1506, 1520	1661	$C_6F_5 \cdot CH_2 \cdot NH_2$	1499, 1515	1653
$C_6F_5 \cdot CH_2Cl$	1515, 1528	1661	$C_6F_5 \cdot CH_2 \cdot CO_2H$ *	1508, 1522	1658
$C_6F_5 \cdot CHCl_2$	1506, 1522	1656	$C_6F_5 \cdot CH_2 \cdot O \cdot CO \cdot CH_3$	1506, 1524	1656

* Mulls in Nujol or hexachlorobutadiene: remainder, liquids.

affords by far the best means of confirming the presence of the ring system. The band at about 1600 cm.$^{-1}$, which was either absent or very weak in compounds derived from pentafluorophenol, probably also arises in ring vibrations, but it is of limited value for identifications.

The bands in the 900—1400 cm.$^{-1}$ (C–F stretching) region in the spectra of compounds containing the pentafluorobenzyl group show considerable variation in strength and position with changes in the side-chain. The strongest band system generally appears at 950—1020 cm.$^{-1}$, but varies considerably in shape and position within this range. Other bands, which sometimes exceed the 950—1020 cm.$^{-1}$ bands in strength, appear at 1110—1140 and 1300—1350 cm.$^{-1}$.

The ultraviolet spectra of pentafluorotoluene and its derivatives show a low-intensity aromatic band at 255—270 mμ. A medium-intensity band in the 220 mμ region is also present in most of the spectra; in some cases (*e.g.*, in the spectrum of pentafluorobenzyl bromide) this band appears only as a weak inflexion on a high-intensity aromatic band, which is moved into the accessible region above 210 mμ by auxochromic substituents.

EXPERIMENTAL

Gas–liquid chromatography was carried out on a Perkin–Elmer No. 154B instrument, calibrated with known mixtures of pure components in each case. Columns (2 m. long × 4 mm. internal diameter) were packed with 30% by wt. of Apiezon " L " grease or silicone " MS 550 " on Celite; the carrier gas was nitrogen and the column temperature was 10° above the mean b. p. of the mixture under investigation. Each mixture was analysed on both columns and the purity of new liquid compounds was established similarly.

n-Butylpentafluorobenzene.—A cold ($-60°$) solution of 0·78M-n-butyl-lithium (62·4 mmoles of Bu^{n}Li) in tetrahydrofuran (80 ml.), prepared from n-butyl chloride,[21] was added to hexafluorobenzene (10·0 g., 53·7 mmoles) in tetrahydrofuran (50 ml.) under nitrogen. The stirred mixture was cooled to $-60° \pm 5°$ throughout the addition (90 min.) and for a further 30 min., then allowed to warm to room temperature and poured, with vigorous stirring, into ice-cold water (200 ml.). The mixture was acidified with 5N-hydrochloric acid until just acid to litmus and extracted with light petroleum (b. p. 30—40°; 3 × 100 ml.), and the extract was dried (MgSO$_4$). Distillation gave n-octane (0·81 g.), b. p. 43—45°/35 mm., $n_D{}^{20}$ 1·3981 (lit.,[22] b. p. 45°/35 mm., $n_D{}^{20}$ 1·3976), and *n-butylpentafluorobenzene* (6·41 g., 53%) (Found: C, 53·3; H, 3·8. $C_{10}H_9F_5$ requires C, 53·6; H, 4·0%), b. p. 84—86°/35 mm., 173—175°/758 mm., $n_D{}^{20}$ 1·4209. A fraction (3·39 g.), b. p. 100—148°/35 mm., was also obtained; this was redistilled and gave a liquid (3·01 g.), b. p. 147—149°/35 mm., which was shown by gas–liquid chromatography to contain n-butylpentafluorobenzene (*ca.* 11%) and an unidentified component (*ca.* 89%). The

[21] Gilman and Gaj, *J. Org. Chem.*, 1957, **22**, 1165.
[22] Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., Amsterdam, 1950, p. 83.

latter was probably *di-n-butyltetrafluorobenzene* (yield ~20%) (Found: C, 63·0; H, 6·3. $C_{14}H_{18}F_4$ requires C, 64·2; H, 6·9%). The total yield of n-butylpentafluorobenzene was 56%.

2,3,4,5,6-*Pentafluorotoluene.*—(a) A cold (−10°) solution of 0·82M-methyl-lithium (0·258 mole of MeLi) in tetrahydrofuran (317 ml.), prepared from methyl chloride,[21] was added to hexafluorobenzene (40·0 g., 0·216 mole) in tetrahydrofuran (200 ml.) under nitrogen. The stirred mixture was cooled to −60° ± 5° throughout the addition (2 hr.) and for 90 min. afterwards. Working up as above gave 2,3,4,5,6-*pentafluorotoluene* (27·9 g., 71%) (Found: C, 46·2; H, 1·7. $C_7H_3F_5$ requires C, 46·1; H, 1·7%), b. p. 117—118°/762 mm., n_D^{20} 1·4023.

(b) No reaction was apparent when 5 ml. of a 1·4M-solution of methyl-lithium in ether were added to hexafluorobenzene (44·5 g., 0·239 mole) in ether (150 ml.) at −50° under nitrogen. The stirred mixture was allowed to warm to −20°; the separation of a black precipitate then showed that reaction was beginning. The remainder of the methyl-lithium solution (157 ml.; 0·226 mole of MeLi total) was added during 2 hr., whilst the mixture was kept at −15° ± 2°. The mixture was stirred at −10° for a further 30 min., allowed to warm to room temperature, and poured into ice-cold water (500 ml.) containing 5N-hydrochloric acid (60 ml.). Separation of the ethereal layer, extraction of the aqueous layer with ether (4 × 100 ml.), and distillation of the dried (MgSO₄) extract gave 2,3,4,5,6-pentafluorotoluene (30·2 g., 69%), identical with the compound described above.

2,3,4,5,6-*Pentafluorotoluene and Aqueous Oxidising Agents.*—No identifiable products were obtained when pentafluorotoluene (1·0 g.) was heated, either under reflux or in sealed tubes at 100—200°, with concentrated nitric acid, 0·5M-potassium permanganate in 1% aqueous sodium carbonate, or M-potassium dichromate in 50% v/v aqueous sulphuric acid.

Pentafluorobenzoic Acid.—A solution of chromium trioxide (3·3 g., 33 mmoles) in water (2 ml.) and glacial acetic acid (5 ml.) was added in 1 hr. to refluxing pentafluorotoluene (1·0 g., 5·5 mmoles) in glacial acetic acid (10 ml.). The mixture was heated under reflux for a further 9 hr., poured into 5N-sulphuric acid (50 ml.), and extracted continuously with light petroleum (b. p. 30—40°) for 24 hr. The extract was washed with 5N-sulphuric acid, dried (MgSO₄), and evaporated, and the residue was recrystallised from toluene–light petroleum (b. p. 100—120°) to give pentafluorobenzoic acid (0·035 g., 3%) (Found: C, 39·5; H, 0·7%; equiv., 210. Calc. for $C_7HF_5O_2$: C, 39·6; H, 0·5%; equiv., 212), m. p. 103—104° (lit., m. p. 106—107°,[7] 103—104°[8]).

Chlorination of 2,3,4,5,6-Pentafluorotoluene.—(a) *With chlorine.* (i) Pentafluorotoluene (4·76 g., 26·2 mmoles) and chlorine (1·86 g., 26·2 mmoles) were sealed, under a vacuum, into a 180-ml. silica tube and irradiated by a 250 w mercury discharge tube for 3 hr. Hydrogen chloride (0·87 g., 91%) (Found: M, 36·8. Calc. for HCl: M, 36·5) was produced. The liquid products were washed from the tube with ether (50 ml.) and the ethereal solution was washed with 2% aqueous sodium carbonate, 2% aqueous sodium sulphite, and water and dried (MgSO₄). Distillation gave pure 2,3,4,5,6-*pentafluorobenzyl chloride* (1·21 g.) (Found: C, 38·8; H, 0·9. $C_7H_2ClF_5$ requires C, 38·8; H, 0·9%), b. p. 156—157°/750 mm., n_D^{20} 1·4432. Chromatographic analysis of the remaining fractions from the distillation showed that the following total yields were obtained: pentafluorotoluene, 1·00 g., 21%; pentafluorobenzyl chloride, 3·56 g., 63%; pentafluorobenzylidene chloride, 0·59 g., 9%; products of b. p. >180°, 0·2 g., 3—4%. The infrared spectrum of the products of b. p. >180° showed the presence of olefinic compounds (strong bands at 1692 and 1724 cm.$^{-1}$) produced by addition of chlorine to the polyfluoroarene ring. (For the spectra of fluorinated cyclohexenes see ref. 3.)

(ii) Pentafluorotoluene (5·55 g., 30·5 mmoles) and chlorine (6·50 g., 91·5 mmoles) were sealed into a 300-ml. silica tube and irradiated, under conditions identical with those of (i) for 20 hr. Hydrogen chloride (2·22 g., 67%) (Found: M, 37·1) was produced, and extraction and distillation of the products as before gave 2,3,4,5,6-*pentafluorobenzylidene chloride* (3·31 g., 43%) (Found: C, 33·6; H, 0·5. $C_7HCl_2F_5$ requires C, 33·4; H, 0·4%), b. p. 62—64°/10 mm., 175—177°/750 mm., n_D^{20} 1·4631. No other aromatic compounds were isolated from this experiment. Redistillation of material boiling above 64°/10 mm. (3·69 g.) gave a fraction (0·54 g.), b. p. 131—133°/16 mm., n_D^{20} 1·4795, with analytical figures corresponding to a tetrachloro(dichloromethyl)pentafluorocyclohexene (Found: C, 21·8; H, 0·4. Calc. for $C_7HCl_6F_5$: C, 21·4; H, 0·3%). The infrared spectrum of this substance showed very weak bands at 1490 and 1527 cm.$^{-1}$ and a strong band at 1695 cm.$^{-1}$. The presence of C–H bonds was shown by a weak band at 3021 cm.$^{-1}$.

(iii) Pentafluorotoluene (5·13 g., 28·2 mmoles) and chlorine (4·01 g., 56·4 mmoles), irradiated for 12 hr., gave hydrogen chloride (1·56 g., 75%) (Found: M, 36·7). Liquid products were distilled and were shown by gas–liquid chromatography to contain pentafluorobenzyl chloride (1·8 g., 30%) and pentafluorobenzylidene chloride (3·2 g., 43%). A fraction (2·03 g., *ca.* 22%), b. p. 110—135°/45 mm., was also obtained, and shown by infrared spectroscopy not to contain aromatic compounds.

(b) *With sulphuryl chloride.* (i) Pentafluorotoluene (5·00 g., 27·5 mmoles), sulphuryl chloride (3·71 g., 27·5 mmoles), and benzoyl peroxide (0·038 g., 0·275 mmole) were heated under reflux for 10 hr. Distillation then gave pentafluorotoluene (3·01 g., 60%), b. p. 116—120°, and a fraction (2·21 g.), b. p. 120—160°, shown by gas–liquid chromatography to contain pentafluorotoluene (10%) and 2,3,4,5,6-pentafluorobenzyl chloride (90%; 34% total yield, 94% on pentafluorotoluene converted).

Under similar conditions toluene itself gives benzyl chloride in 80% yield after only 30 minutes' refluxing.[9]

(ii) Sulphuryl chloride (7·42 g., 55 mmoles) and benzoyl peroxide (0·152 g., 1·1 mmoles) were added in portions to pentafluorotoluene (5·0 g., 27·5 mmoles), heated under reflux for 44 hr. Distillation then gave sulphuryl chloride (0·91 g., 12%), b. p. 69—70°, and a fraction (4·97 g.), b. p. 158—160°, shown by gas–liquid chromatography to contain 2,3,4,5,6-pentafluorobenzyl chloride (92%; 77% yield from pentafluorotoluene) and 2,3,4,5,6-pentafluorobenzylidene chloride (8%; 7% yield from pentafluorotoluene).

2,3,4,5,6-*Pentafluorobenzyl Bromide.*—Bromine (15·0 g., 94·0 mmoles) was added in 75 min. to pentafluorotoluene (15·0 g.; 82·5 mmoles), heated under reflux on a bath at 140° and irradiated by a 100 w bulb. Heating and irradiation were continued for a further 30 min., and the mixture was then cooled, dissolved in ether (50 ml.), and washed with 1% aqueous sodium hydroxide (50 ml.), 2% aqueous sodium sulphite (25 ml.), and water (50 ml.). The dried (MgSO$_4$) ethereal solution was distilled to give pentafluorotoluene (0·76 g., 5%), b. p. 116—119°, and 2,3,4,5,6-*pentafluorobenzyl bromide* (16·9 g., 85%) (Found: C, 32·3; H, 0·9. C$_7$H$_2$BrF$_5$ requires C, 32·2; H, 0·8%), b. p. 175—177°/761 mm., n_D^{20} 1·4710.

S-(2,3,4,5,6-*Pentafluorobenzyl)thiouronium Picrate.*—Pentafluorobenzyl chloride (0·2 g.) and thiourea (0·1 g.) in ethanol (2 ml.) were heated under reflux for 90 min. Picric acid (0·25 g.) was added, refluxing was continued for 15 min., and the mixture was diluted with water (1 ml.) and kept for 1 hr. The yellow needles which separated were recrystallised from water and gave the *thiouronium picrate* (0·32 g., 60%) (Found: C, 34·7; H, 1·7; N, 14·4. C$_{14}$H$_8$F$_5$N$_5$O$_7$S requires C, 34·6; H, 1·7; N, 14·4%), m. p. 167—168°. Application of the above procedure to pentafluorobenzyl bromide gave the thiouronium picrate in 80% yield.

Reaction of 2,3,4,5,6-Pentafluorobenzyl Bromide with Aqueous Alkali.—The bromide (5·00 g., 19·2 mmole) was heated under reflux with potassium hydroxide (1·11 g., 19·8 mmoles) in water (30 ml.) for 5 hr. Titration of a portion of the aqueous phase then showed that the theoretical quantity of alkali had been consumed; this phase also gave a positive test for bromide and for fluoride. The mixture was extracted with ether (4 × 25 ml.) and the extracts were washed with water, dried (MgSO$_4$), and evaporated. The residue (3·51 g.) was recrystallised several times from n-hexane and gave white crystals (1·82 g.), m. p. 102—104°, the elemental analysis for which was consistent with the structure, C$_6$F$_5$·CH$_2$·O·C$_6$F$_4$·CH$_2$·O·C$_6$F$_4$·CH$_2$·OH (Found: C, 45·6; H, 1·5. C$_{21}$H$_7$F$_{13}$O$_3$ requires C, 45·5; H, 1·3%). Its infrared spectrum showed strong bands at 941 (C–F stretching) and 1502 cm.$^{-1}$ (aromatic ring vibrations); a weak broad band centred on 3344 cm.$^{-1}$ showed the presence of hydroxyl groups. Comparison with the spectrum of 2,3,4,5,6-pentafluorobenzyl alcohol showed that this compound was not present.

2,3,4,5,6-*Pentafluorobenzyl Acetate.*—Pentafluorobenzyl bromide (4·00 g., 15·3 mmoles), freshly fused, finely powdered potassium acetate (1·80 g., 18·4 mmoles), and glacial acetic acid (1·8 ml.) were heated under reflux (bath 180—200°) for 6 hr. The mixture was poured into water (50 ml.) and extracted with light petroleum (b. p. 30—40°; 3 × 50 ml.), and the extract was washed with 2% aqueous sodium hydroxide (50 ml.) and water (50 ml.), and dried (MgSO$_4$). Distillation gave 2,3,4,5,6-*pentafluorobenzyl acetate* (3·13 g., 83%) (Found: C, 45·1; H, 2·3. C$_9$H$_5$F$_5$O$_2$ requires C, 45·0; H, 2·1%), b. p. 201°/761 mm., n_D^{20} 1·4305; its carbonyl absorption is at 1751 cm.$^{-1}$.

The acetate (2·00 g.) was heated under reflux with 40% v/v aqueous sulphuric acid for 6 hr., and the mixture was then poured into water and extracted with light petroleum (b. p. 30—40°; 3 × 50 ml.). The extract was dried (MgSO$_4$) and distilled to give a fraction (0·94 g.), b. p.

190—193°, shown by infrared spectroscopy and gas–liquid chromatography to contain unchanged acetate (48%) and 2,3,4,5,6-pentafluorobenzyl alcohol (62%, 35% yield).

(Pentafluorophenyl)acetic Acid and 1,2-Bispentafluorophenylethane.—Pentafluorobenzy bromide (2·09 g., 8·0 mmoles) in ether (8 ml.) was added, at a rate sufficient to maintain refluxing, to magnesium (0·39 g., 0·016 g.-atom) and a small crystal of iodine in ether (2 ml.). The mixture was heated on a water-bath for 1 hr., then cooled, and the ethereal solution was decanted, carbonated by the addition of solid carbon dioxide (5 g.), and poured on ice (10 g.) and concentrated hydrochloric acid (1 ml.). The ethereal layer was separated and the aqueous phase was extracted with ether (2 × 20 ml.). The combined extracts were extracted with aqueous 2N-sodium hydroxide (2 × 20 ml.), dried ($MgSO_4$), and evaporated. The residue was recrystallised from ethanol to give prisms of *1,2-bispentafluorophenylethane* (0·86 g., 59%) (Found: C, 46·3; H, 1·3. $C_{14}H_4F_{10}$ requires C, 46·4; H, 1·1%), m. p. 107—108° (sintered 104°). The alkaline extract was acidified with 5N-hydrochloric acid (40 ml.) and extracted continuously with ether for 24 hr. The extract was dried ($MgSO_4$) and evaporated, and the residue was purified by sublimation *in vacuo* and gave *(pentafluorophenyl)acetic acid* (0·24 g., 14%) (Found: C, 42·8; H, 1·5%; equiv., 224. $C_8H_3F_5O_2$ requires C, 42·5; H, 1·3%; equiv., 226), m. p. 108—110°; its carbonyl absorption is at 1712 cm.$^{-1}$.

The acid (0·10 g.) was dissolved in warm water and neutralised with sodium hydroxide, and the pH was adjusted to 4 with hydrochloric acid. An aqueous solution of *S*-benzylthio-uronium chloride was added, the mixture was left at 5° overnight, and the derivative which separated was recrystallised from aqueous ethanol to give colourless plates of S-*benzylthio-uronium (pentafluorophenyl)acetate* (0·12 g.) (Found: C, 49·1; H, 3·5. $C_{16}H_{13}F_5N_2O_2S$ requires C, 49·0; H, 3·3%), m. p. 162—163°.

2,3,4,5,6-Pentafluorobenzylamine.—Pentafluorobenzyl bromide (10·0 g., 38·3 mmoles) and potassium phthalimide (7·10 g., 38·3 mmoles) were heated under reflux (bath 190—200°) for 44 hr. The mass was cooled at intervals of about 6 hr. and powdered to ensure thorough mixing of the reactants. The product was ground in a mortar under water (50 ml.) and separated by filtration, and the filtrate was shown to contain considerable bromide and some fluoride ion. The residue was washed with water until the washings were free from bromide, dried, and recrystallised several times from ethanol, to give *N-(2,3,4,5,6-pentafluorobenzyl)-phthalimide* (8·75 g., 70%) (Found: C, 55·2; H, 2·0; N, 4·4. $C_{15}H_6F_5NO_2$ requires C, 55·1; H, 1·8; N, 4·3%) as white needles, m. p. 108—110°.

The substituted phthalimide (14·70 g., 45·0 mmoles), suspended in ethanol (37·5 ml.), was heated under reflux with 80% w/w hydrazine hydrate (2·81 g., containing 1·44 g., 45·0 mmoles, of N_2H_4) for 1 hr. 5N-Hydrochloric acid (75 ml.) was added, refluxing was continued for a further 30 min., and the mixture was cooled and filtered to remove phthalhydrazide. The filtrate was concentrated to about 60 ml., then refiltered, and aqueous 5N-potassium hydroxide (100 ml.) was added slowly, with cooling in ice. The oil which separated was extracted with light petroleum (b. p. 30—40°; 6 × 50 ml.), and the extract was dried and distilled to give a colourless liquid (7·31 g.), b. p. 167—169°, containing a fine white suspension. Filtration and redistillation under reduced pressure gave *2,3,4,5,6-pentafluorobenzylamine* (6·72 g., 76%) (Found: C, 42·8; H, 2·2; N, 7·1%; equiv., 197. $C_7H_4F_5N$ requires C, 42·6; H, 2·0; N, 7·1%; equiv., 197) as a clear, colourless, mobile liquid, b. p. 89—90°/50 mm., 168—169°/768 mm. (slight decomp.), n_D^{20} 1·4407. The presence of the NH_2 group was shown by a doublet at 3289, 3378 cm.$^{-1}$.

No change took place when the pure amine was distilled at 50 mm., but distillation at atmospheric pressure resulted in the appearance of a white suspension in the colourless distillate. The solid was soluble in water, which afterwards gave a positive test for fluoride ion. A sample of the pure amine was stored in a sealed tube at −78° for 8 weeks and remained clear and colourless; when kept at room temperature for 12 months, the sample was completely solid.

The amine (0·20 g.) was shaken with benzoyl chloride and 10% aqueous sodium hydroxide, and the resulting solid recrystallised from ethanol as colourless plates of *N-benzoyl-2,3,4,5,6-pentafluorobenzylamine* (0·22 g.) (Found: C, 55·7; H, 2·6; N, 4·8. $C_{14}H_8F_5NO$ requires C, 55·8; H, 2·7; N, 4·7%), m. p. 180·5°. Its carbonyl absorption is at 1642 cm.$^{-1}$.

Ionisation Constant of 2,3,4,5,6-Pentafluorobenzylamine.—This was determined by potentio-metric titration of 0·01N-solutions of the amine in carbonate-free distilled water against 0·01N-hydrochloric acid. The apparatus has been described earlier.[20] Repeated determinations

at the " half-neutralisation " point at 25° gave pH = pK_a = 7·70, whence pK_b = 6·30, K_b = 5·0 × 10⁻⁷.

Reaction of 2,3,4,5,6-Pentafluorobenzylamine with Nitrous Acid.—The amine (2·566 g., 13·03 mmoles) was neutralised with 1·516N-hydrochloric acid (8·66 ml.) and cooled in ice. Finely powdered sodium nitrite (1·00 g., 14·5 mmole) and ether (10 ml.) were added, and the mixture was shaken for 20 min. with periodic cooling. No reaction was evident; the ether

TABLE 4. *Ultraviolet spectra.*

	In hexane				In ethanol			
	$\lambda_{max.}$ (mμ)	ε	$\lambda_{min.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	$\lambda_{min.}$ (mμ)	ε
$C_6F_5 \cdot CH_3$	220·5	1620	214	1520	220·5	1560	214·5	1440
	258·5	300	241	110	258·5	290	242	130
$C_6F_5 \cdot C_4H_9^n$ †	219·5	1920	216	1910	220	1850	215·5	1780
	258·5	330	242	130	258	320	242	155
$(C_6F_5 \cdot CH_2 \cdot)_2$	219 *	6100	241	275	219	5300	242	310
	260	8200			260	800		
$C_6F_5 \cdot CH_2Cl$ †	219 *	5500	243	145	219 *	5500	243	160
	266	760			266	750		
$C_6F_5 \cdot CHCl_2$	211	8300	243	155	211	9000	244	175
	217 *	6900			217 *	7500		
	269	980			269	980		
$C_6F_5 \cdot CH_2Br$	212	9200	259	900	212·5	9600	259	850
	222 *	7300			221 *	7800		
	266	930			266	880		
$C_6F_5 \cdot CO_2H$ †	217 *	2450	240	130	217 *	2650	242·5	200
	261	530			260	460		
$C_6F_5 \cdot CH_2 \cdot NH_2$	212	4470	246	230	260	450	244	220
	260	420						
$C_6F_5 \cdot CH_2 \cdot O \cdot CO \cdot CH_3$ †	263·5	740	240	130	263·5	720	240	140

* = Inflexion. † These compounds show indications of strong bands in the region 200—210 mμ.

layer was separated and stored in a container cooled in ice. The aqueous layer was cooled to 4—5°, and a further 10 ml. of ether and 2 drops of 10% aqueous sulphuric acid were added: immediate effervescence occurred, and the mixture was shaken for 10 min., a yellow-green colour appearing in the ether layer. The layers were separated as before, and the procedure was repeated until no colour was transferred to the ether. The combined extracts (*ca.* 90 ml.) were washed with 2% aqueous sodium carbonate, dried (MgSO₄), and distilled under reduced pressure to give 2,3,4,5,6-pentafluorobenzyl chloride (0·64 g., 23%), b. p. 78—79°/50 mm., identified by infrared spectroscopy, and 2,3,4,5,6-*pentafluorobenzyl alcohol* (0·72 g., 28%) (Found: C, 42·0; H, 1·6. $C_7H_3F_5O$ requires C, 42·4; H, 1·5%), b. p. 109—110°/50 mm., which crystallised as needles, m. p. 33—35°. The infrared spectrum of the alcohol (melt) showed a broad hydrogen-bonded OH band at 3340 cm.⁻¹ and a sharp " free " OH band at 3610 cm.⁻¹.

The alcohol has been obtained previously,[7] as a product of the reduction of pentafluorobenzoic acid with lithium aluminium hydride, but it was not isolated.

Ultraviolet Spectra.—These were measured (Table 4) in solution, in hexane and in ethanol, over the range 210—450 mμ, with a Unicam S.P. 500 instrument.

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